

FORM PTO-1390 (Modified)
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ATTORNEY'S DOCKET NUMBER

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

6235-16-DCL

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

10/088049

INTERNATIONAL APPLICATION NO.
PCT/EP00/07980

INTERNATIONAL FILING DATE
August 16, 2000

PRIORITY DATE CLAIMED
September 18, 1999

TITLE OF INVENTION

PROCESS FOR THE IMPROVEMENT OF THE WATER QUALITY OF MAINTENANCE WATERS

APPLICANT(S) FOR DO/EO/US

RITTER, Gunter

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☐ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☒ Certificate of Mailing by Express Mail
23. ☐ Other items or information:

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 10/088049	INTERNATIONAL APPLICATION NO. PCT/EP00/07980	ATTORNEY'S DOCKET NUMBER 6235-16-DCL
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24. The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :				CALCULATIONS PTO USE ONLY	
<input type="checkbox"/>	Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO	\$1040.00			
<input checked="" type="checkbox"/>	International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO	\$890.00			
<input type="checkbox"/>	International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO	\$740.00			
<input type="checkbox"/>	International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4)	\$710.00			
<input type="checkbox"/>	International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4)	\$100.00			
ENTER APPROPRIATE BASIC FEE AMOUNT =			\$890.00		
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).			\$0.00		
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	18 - 20 =	0	x \$18.00	\$0.00	
Independent claims	2 - 3 =	0	x \$84.00	\$0.00	
Multiple Dependent Claims (check if applicable). <input type="checkbox"/>				\$0.00	
TOTAL OF ABOVE CALCULATIONS =				\$890.00	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27). The fees indicated above are reduced by 1/2.				\$0.00	
SUBTOTAL =				\$890.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).				\$0.00	
TOTAL NATIONAL FEE =				\$890.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). <input type="checkbox"/>				\$0.00	
TOTAL FEES ENCLOSED =				\$890.00	
				Amount to be:	\$
				refunded	
				charged	\$

- a. ☐ A check in the amount of _____ to cover the above fees is enclosed.
- b. ☒ Please charge my Deposit Account No. **23-0450** in the amount of **\$890.00** to cover the above fees. A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **23-0450** A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

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CERTIFICATE OF MAILING BY "EXPRESS MAIL" (37 CFR 1.10)

Applicant(s): **Gunter Ritter**

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6235-16-DCL

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Not yet assigned

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Not yet assigned

Invention:

PROCESS FOR THE IMPROVEMENT OF THE WATER QUALITY OF MAINTENANCE WATERS

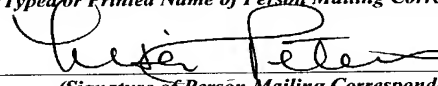
I hereby certify that this Trans. Ltr. to the US Designated/Elected Office filing under 35 U.S.C. 371
(Identify type of correspondence)

is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 in an envelope addressed to: The Commissioner of Patents and Trademarks, Washington, D.C.

20231-0001 on 3/11/02
(Date)

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**Process for the improvement of the water quality of
maintenance waters**

The invention concerns individual processes for the improvement of the water quality or correction and adjustment of important chemical water parameters of biological maintenance systems with use of ecologically neutral, chemically- and microbiologically-acting water additives, a combination of several processes for the improvement of the water quality in biological maintenance systems, as well as a single or multiple component product hereby usable.

In biological maintenance systems, e.g. aquaria, aquatic terrains and garden ponds, due to the daily feeding of the fish and other aquatic animals kept therein, it results in cumulative changes of important chemical water parameters and consequently in a continuous impairment of the water quality. From this follows a correspondingly reduced quality of life of the maintained fish and other aquatic animals.

If the starting water, e.g. tap water, possesses a sufficient quality, then, by frequent partial or complete change of water, an impairment of the water quality caused by the maintenance can be countered. The procedure of the water change is laborious and unpleasant for the aquarianists, for the maintained fish and other aquatic organisms not without, in part, considerable endangering due to undesired properties

of the fresh starting water, such as for example chlorine or heavy metals.

Consequently, a minimising of the water change frequency and amount would be desirable. when - as described in the present invention - it succeeds to suppress or to eliminate the impairment of the water quality.

In detail, it comes, in biological maintenance systems, to the following changes of important water parameters impairing the water quality. This is countered, in part, by already known measures.

A) An example for such changes is the increase of the phosphate concentration by continuous introduction with the feed. The phosphate increase to values above 10 - 20 mg/l is disadvantageous since the undesired algal growth is promoted by phosphate.

The following measures are known for the phosphate reduction:

- a) Binding of phosphate to Al^{3+} and/or Fe^{3+} oxides (hydroxide group-containing granulates) which are introduced into the filter system. Disadvantageous is their limited capacity. After their exhaustion, it is necessary to change the granulates, which is frequently very laborious. If the aquarianist does not regularly measure the phosphate content, he will not recognise the exhaustion of the material and the PO_3^{3-} concentration in the maintenance water will

again increase, i.e. the treatment success of this method is frequently only insufficient.

- b) In the case of regular use, the addition of dissolved inorganic Al^{3+} and/or Fe^{3+} salts also leads to a lowering of the PO_4^{3-} concentration. Disadvantages of this process are:

- high fish toxicity of the dissolved inorganic Al^{3+} and Fe^{3+} salts,
- enrichment of the water with anions, such as e.g. chloride and sulphate,
- reduction of the carbonate hardness, of the HCO_3^- and CO_3^{2-} content and thus
- reduction of the buffer capacity,
- lowering of the pH level and danger of the acid fall at $\text{KH} = 0^\circ \text{dH}$,
- turbidity of the water and unpleasant flocculation of $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$.

- B) A further example for the said undesired changes is the increase of the nitrate concentration by continuous introduction of proteins and other sources of nitrogen with the feed. All sources of nitrogen originating from the feed, to the greater part proteins, are oxidised microbially via ammonia and nitrite to nitrate. The continuous nitrite increase represents an unnatural loading of the maintenance water which is undesired for the aquarianist. Frequently, the nitrate content of the starting water is already so high, e.g. at 25 - 50 mg/l, so that the natural NO_3^- concentration of a few mg/l is never achievable by change of water.

The following measures are known for the lowering of the nitrate content:

- a) Lowering of the nitrate content by anion exchangers, mostly in chloride form. Disadvantageous is hereby the replacement of the nitrate ions by the loading anions of the exchanger, mostly chloride, and the replacement of sulphate and hydrogen carbonate ions. Besides the undesired lowering of the carbonate hardness, the chemical water composition is completely changed.
- b) Denitrification in anaerobic medium or in anaerobic reactors. By introduction of practically insoluble, biologically decomposable organic, nitrogen-free material in granulate form into the filter system, by means of strong O_2 provisions, anaerobic regions are provided in which nitrate, as source of oxygen, is reduced to N_2 . Disadvantageous is:
 - the uncertain dosing,
 - the uncertain process control and process controllability,
 - the sulphate reduction to be expected in the case of small NO_3^- concentrations to highly toxic hydrogen sulphide.
- c) The lowering of the carbonate hardness caused by nitrification forms a further example for the mentioned undesired water changes. The oxidation of the continuously supplied organic nitrogen proceeds via the oxidation of ammonia to nitrite made possible by nitrifying bacteria. In the case of this biological process, one mol H^+ ions

result per mol of ammonia. The liberated H^+ ions react with bases present, mostly hydrogen carbonate as former of the carbonate hardness, with protonisation and reduction of the carbonate hardness.

For the compensation of the carbonate hardness losses (or HCO_3^- losses) but also for the increasing of the carbonate hardness, the following measures are known:

- a) Addition of $NaHCO_3$ and/or Na_2CO_3 as powder or as solution. The process functions dependably but involves the following disadvantages:
 - In the case of $NaHCO_3/Na_2CO_3$ mixtures, it results in rapid pH increases in the maintenance water which lead to considerable stress of the organisms.
 - In waters with increased ammonium contents, parallel to the pH increase inter alia a lethal amount of ammonia is liberated.
 - The water solubility of $NaHCO_3$ is relatively low so that highly concentrated liquid products with convenient use are not possible.
- b) Addition of freshly prepared solutions which, besides dissolved calcium hydrogen carbonate, also contain much free CO_2 . The excess CO_2 can lead to a rapid CO_2 damaging of the organisms. Besides the HCO_3^- concentration, the Ca^{2+} concentration is here also increased, which is not always desired.

Furthermore, chemically and biologically caused losses of dissolved calcium hydrogen carbonate can bring about

undesired water changes. Due to CO_2 consumption and the pH increase connected therewith, the lime/carbonic acid equilibrium is displaced in the direction of lime precipitation. The disadvantageous loss of dissolved $\text{Ca}(\text{HCO}_3)_2$ leads to a corresponding lowering of the calcium concentration and of the HCO_3 concentration (carbonate hardness lowering).

For the compensation of the losses of $\text{Ca}(\text{HCO}_3)_2$ or its increasing, the following measures are known:

- a) Addition of solutions which, besides $\text{Ca}(\text{HCO}_3)_2$ still contain free CO_2 . This measure is encumbered with the above-described disadvantages. A further disadvantage lies in the laboriousness of the process since the $\text{Ca}(\text{HCO}_3)_2$ solutions must be laboriously prepared by dissolving of CaCO_3 or $\text{Ca}(\text{OH})_2$ in CO_2 -enriched water. By addition of $\text{Mg}(\text{OH})_2$ or $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2$ a solution can also be prepared which contains additional $\text{Mg}(\text{HCO}_3)_2$.
- b) Addition of solid mixtures which contain equivalent amounts of NaHCO_3 and soluble Ca, Mg salts (mostly chlorides). By dissolving of these mixtures in maintenance water, the ions $\text{Ca}^{2+} + 2 \text{Cl}^- + 2 \text{Na}^+ + 2 \text{HCO}_3^-$ are introduced. Besides the desired $[\text{Ca}^{2+} + 2 \text{HCO}_3]$, the water now contains the equivalent amount of NaCl (or also Na_2SO_4), which is undesired. The disadvantage of this process consists in the introduction of foreign salts, e.g. NaCl or Na_2SO_4 .

Finally, a consumption of dissolved carbon dioxide also changes the water quality.

The various described problems initially appear to be heterogenous and not solvable with one principle.

Surprisingly, however, for all partial problems there exists a common solution which includes the following chemical and microbiological principles:

- Utilisation of the microbiological activity of the water and especially of the filter systems in the maintenance systems which include the aerobic and anaerobic processes.
- Use of components, products and compositions which are biologically decomposable in part or completely.
- Linkage of microbiological and chemical processes in the maintenance system.
- Use of components, products and compositions which not only fulfil the desired function but introduce no undesired additional materials or allow them to accumulate.
- Use of components, products and compositions which are completely safe for fish and other aquatic organisms.
- All products and methods behave ecologically neutral and lead to no secondary impairments of the water quality.
- All promoting functions are alone very simple to handle and make possible dosed water additions.

Thus, the subject of the invention is a process for the improvement of the water quality of biological maintenance systems, which is characterised in that to the maintenance system one adds singly or in combination

- a) for the lowering of the phosphate concentration, at least one easily or sparingly soluble Al^{3+} , Fe^{3+} , TiO^{2+} , ZrO^{2+} or Ca^{2+} salt of an organic carboxylic acid, possibly in admixture with an organic carboxylic acid;
- b) for the lowering of the nitrate concentration or limitation of the nitrate increase, at least one water-soluble N-free, biologically decomposable organic compound;
- c) for the increasing of the carbonate hardness or of the HCO_3^- concentration, at least one alkali metal or alkaline earth metal salt of an organic acid;
- d) for the increasing of the total hardness or of the concentration of Ca^{2+} and Mg^{2+} hydrogen carbonates, a mixture of at least one Ca^{2+} and Mg^{2+} salt of an organic carboxylic acid and for the increasing of the CO_2 concentration, at least one biologically decomposable compound.

Furthermore, the subject of the invention is a single or multiple component product for the improvement of the water quality of maintenance systems for the functional, causal use according to need, characterised by a content (singly or in combination) of

- 1.) at least one easily or sparingly soluble Al^{3+} , Fe^{3+} , TiO^{2+} , ZrO^{2+} or Ca^{2+} salt of an organic carboxylic acid, possibly in admixture with an organic carboxylic acid;

- 2.) at least one water-soluble, N-free biologically decomposable organic compound;
- 3.) at least one soluble alkali metal or alkaline earth metal salt of an organic carboxylic acid, and
- 4.) a mixture of at least one Mg^{2+} and Ca^{2+} salt of an organic carboxylic acid.

The consistent use and linking of the maintenance system as microbiological and chemical reactors for the achievement of the desired water improvement from simple added precursors is novel and also not obvious for the expert and, because of the simplicity, of the controllabl and commanding processes and of the complete absence of potentially damaging side effects and actions, brings considerable and innovative advantages in comparison with the solutions of the prior art. An especial advantage of the invention is also to be seen in the fact that it makes possible a separate or common solution of the described partial problems.

In the following, the detailed solutions according to the invention are described:

A) Lowering of the phosphate concentrations

This preferably takes place with salts of Al^{3+} , Fe^{3+} and TiO^{2+} or ZrO^{2+} with organic carboxylic acids, e.g. with their acetates, formates, tartrates and especially citrates, Besides the strongly phosphate-binding metal ions Al^{3+} , Fe^{3+} , TiO^{2+} , ZrO^{2+} , there can also be used calcium salts of organic carboxylic acids in similar manner, however with considerably

smaller phosphate elimination ability. Mixtures of salts of organic acids with the basic organic acids and other organic acids are also usable with the same effect, e.g.

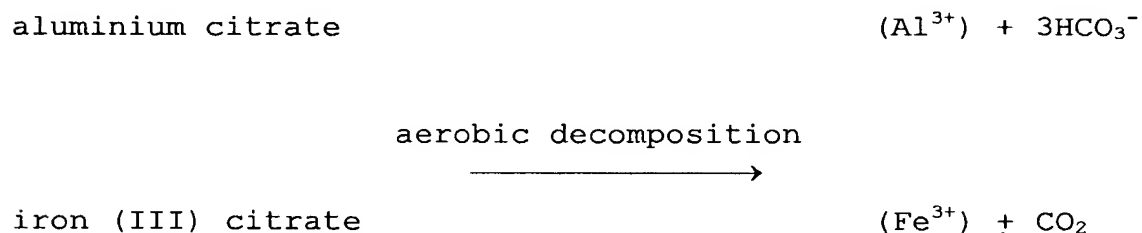
aluminium citrate plus citric acid,

iron (III) citrate plus citric acid,

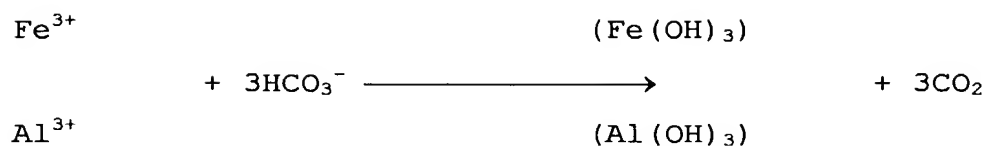
iron (III) citrate plus tartaric acid.

Furthermore, it is also possible to add sparingly-soluble salts of the said metals with organic acids in solid form (powder, granulate, tablets) as depot phosphate eliminators to the filter system or generally to the maintenance system.

The principle is illustrated in the following for Al^{3+} and Fe^{3+} salts but applies correspondingly also for TiO^{2+} and ZrO^{2+} salts. If Al^{3+} and/or Fe^{3+} salts of carboxylic acids are added to the maintenance water, initially no flocculation and turbidity is observed. Only in the case of aerobic biological decomposition in the filter system according to



In the case of direct subsequent formation of $\text{Al}(\text{OH})_3$ or $\text{Fe}(\text{OH})_3$ according to



is phosphate added on and precipitated out together with the hydroxides.

The metal hydroxides precipitated out with co-flocculated phosphate collect in the filter sludge and are eliminated in the case of the regular filter cleaning.

By means of regular addition of organic metal salts, e.g. as aqueous solution, to the maintenance water, the phosphate increase can be completely prevented.

In contradistinction to the phosphate precipitation with inorganic Al^{3+} or Fe^{3+} salts, the phosphate precipitation according to the invention contains serious and surprising advantages:

- no turbidity and flock formation results in the water,
- the process takes place substantially in the biologically-active filter system,
- the organic metal salts behave
 - toxicologically neutral,
 - ecologically neutral,
 - carbonate hardness neutral,
- no enriching foreign ions are added,
- by aerobic decomposition of carboxylic acid anions, only CO_2 is produced, which positively influences the CO_2 content or compensates the CO_2 consumption in part.

The resulting phosphate concentrations are typical for each metal:

for Fe citrate: about 0.0 - 0.2 mg/l,
for Al citrate: about 0.0 - 0.5 mg/l,
for Ca citrate: about 0.5 - 1.5 mg/l.

Very good phosphate elimination successes are achieved when, weekly or two weekly; 1 mg/l to 100 mg/l, preferably 10 mg/l to 40 mg/l aluminium citrate, iron citrate or their mixtures are added to the maintenance water. The phosphate elimination action is dependent upon the introduced amount of metal cation.

B) Lowering of the nitrate concentration or limitation of the NO_3 increase by N-free, soluble organic compounds.

If N-free, organic, decomposable substances are added regularly to the maintenance water, also without the presence of anaerobic reactors, the increase of the nitrate concentration is slowed down or limited and a nitrate concentration is achieved which levels out at an average level. Without treatment with these water additives according to the invention, the nitrate content increases ever further monotonously and unlimitedly. Since the reason for the hindered or limited nitrate increase lies in a partial denitrification in the anaerobic microregions in the filter, parallel to the slowing down, limitation of the nitrate increases, the nitrification-caused loss of carbonate hardness (HCO_3^- concentration) is also inhibited or limited.

As nitrate-reducing, water-soluble compounds, in principle all biologically decomposable organic compounds can be used

but preferably aliphatic compounds, such as for example alcohols; e.g. glycerol, sorbitol, ethanol, sugars, e.g. pentoses, hexoses, saccharose, carboxylic acids, e.g. acetic Acid, citric acid, lactic acid and tartaric acid.

Combinations of in each case equal part amounts of citric acid and saccharose or acetic acid and saccharose have also proved to be very useful.

If, to the maintenance water, one adds three times a week or every two days 5 - 100 mg/l, preferably 5 - 40 mg/l of the acid compounds or mixtures, then the nitrate increase is slowed down and, in relation to the selected dosing, definite nitrate highest concentrations are no longer exceeded.

Dosing examples for the combination citric acid/saccharose are:

- a) 3 dosings per week with 10 mg/l [citric acid plus saccharose (1:1)]: nitrate limiting concentration: 60 - 80 mg/l
- b) 3 dosings per week with 20 mg/l [citric acid plus saccharose (1:11)]: 40 mg/l.

In the case of higher dosings, e.g. 60 - 100 mg/l three times weekly or more frequent lower dosings, e.g. daily 10 mg/l, the nitrate limiting concentration can be lowered still further, e.g. to 5 - 10 mg/l NO_3^- .

Parallel to the NO_3^- stabilisation, there is also achieved a stabilisation of the carbonate hardness at minimum values below which the carbonate hardness does not sink further.

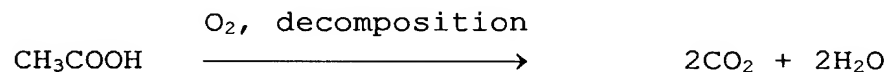
The added compounds are completely broken down to H_2O and CO_2 . The CO_2 formed is used by plants, algae and nitrifying bacteria as C-source.

By introduction of an aeration, the CO_2 concentration, can be corrected downwardly according to need.

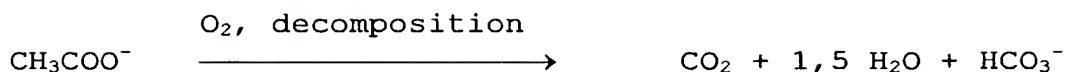
C) Increasing of the carbonate hardness or of the HCO_3^- concentration

In the case of the solution according to the present invention, one makes use of the following microbiological/chemical principle with the use of Na^+ , Ca^{2+} , Mg^{2+} and Sr^{2+} salts of aliphatic carboxylic acids, such as e.g. acetic acid, lactic acid, citric acid, tartaric acid, formic acid, propionic acid, malic acid and the like.

If carboxylic acids, e.g. acetic acid, are decomposed microbiologically, there results only H_2O and CO_2 :



If, on the other hand, one subjects salts of the carboxylic acids to the microbiological decomposition, then, besides CO_2 corresponding to the number of the introduced negative charges of the anions, hydrogen carbonate is also formed:



By the introduction of salts of carboxylic acids into the maintenance water, after biological decomposition, the hydrogen carbonates are formed.

On the example for sodium hydrogen carbonate from organic sodium salts, e.g. Na acetate, Na citrate, this may not act very spectacularly since NaHCO_3 itself is easily accessible. However, even here, in the case of liquid composition, the great advantage exists of the mostly - in comparison with NaHCO_3 - very high solubility, for example Na acetate which permit high product concentrations and ranges.

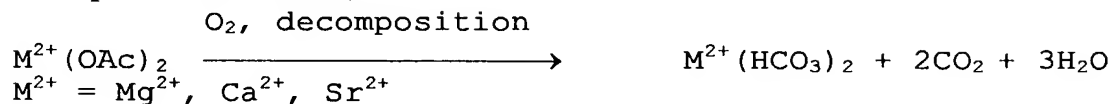
A further advantage of the use of organic Na salts instead of NaHCO_3 or Na_2CO_3 consists in the pH neutral use:

- The Na salt of organic acids acts pH neutral, with excess carboxylic acid(s) can even be adjusted acidic in the product. This is naturally not possible with NaHCO_3 or Na_2CO_3 .
- In the case of biological decomposition (apart from in the case of formates), CO_2 still results which also counters a pH increase.

The advantages of the problem solution according to the invention are still better recognisable when one considers the introduction of the hydrogen carbonates of the alkaline earth metal, Mg^{2+} , Ca^{2+} , Sr^{2+} which, as known, are not available as substances. By addition of the soluble Mg^{2+} , Ca^{2+} , Sr^{2+} salts of organic carboxylic acids, the desired

concentrations of the hydrogen carbonates can be built up in the maintenance water without problems.

Example: (acetate)



The dosing is orientated to the desired adjustment or increase of the carbonate hardness or of the HCO_3^- concentration. 1 mMol/l Na salt of organic carboxylic acids increases the carbonate hardness by 2.8°dH, 1 mmol/l Mg^{2+} , Ca^{2+} , Sr^{2+} salts of organic carboxylic acids increases the carbonate hardness by 5.6°dH.

The alkali metal or alkaline earth metal salts of the organic carboxylic acids can be added to the maintenance water in solid form (powder, granulate, tablets) or in the form of aqueous solutions.

As carboxylic acids, there can be used:

a) for Na^+ salts:

practically all aliphatic carboxylic acids, especially acetic acid, lactic acid, citric acid, tartaric acid and the like.

b) for Mg^{2+} salts:

practically all aliphatic carboxylic acids, especially acetic acid, lactic acid, citric acid, tartaric acid and the like.

- c) for Ca^{2+} salts:
all aliphatic carboxylic acids which form water-soluble Ca^{2+} salts, especially formic acid, acetic acid, propionic acid, lactic acid, malic acid and the like.
- d) for Sr^{2+} salts:
all aliphatic carboxylic acids which form water-soluble Sr^{2+} salts, especially formic acid, acetic acid, propionic acid, lactic acid, malic acid and the like.
- D) Increasing of the total hardness or of the concentration of Ca^{2+} and Mg^{2+} hydrogen carbonates

The principle of this problem solution according to the invention and all important details of use were described under C). The advantages of the method and of the composition are:

- very simple and sure, defined adjustment and increase of the total hardness,
- problem-free preparation and use of product compositions, especially liquid solutions,
- no introduction of undesired foreign ions,
- easy adjustment of all desired Mg:Ca ratios from $\infty:1$ to $1:\infty$.

- only controlled amounts of CO_2 are produced which serve for the C-supply for plants, algae and autotrophic micro-organisms.
- besides the here-described Mg^{2+} and Ca^{2+} hydrogen carbonates formed from organic salts, other inorganic Mg^{2+} , Ca^{2+} salts, such as e.g. chlorides or sulphates, can also be added in combination so that every possible or required chemical composition of the total hardness can be realised.

E) Increasing of the CO_2 concentration

In the preceding problem solutions A) to D), it has already been described that, In the case of the biological breakdown of organic compounds, CO_2 is formed in the maintenance system. This can be built up to an internal, microbiologically-working CO_2 supply system. A continuous and sufficient but still not organism-damaging supply of CO_2 to the maintenance water fulfils various important functions:

- carbon fertilising of the plant organisms,
- carbon supplying of the autotrophic micro-organisms, especially of the nitrificants,
- prevention of the pH increase caused by CO_2 consumption,
- adjustment of a definite pH value by adjustment of the $\text{HCO}_3^-/\text{CO}_2$ acid-base equilibrium,

- intervention in the lime/CO₂ equilibrium and prevention of the chemical and biological lime precipitation.

It has been shown that CO₂ concentrations between 1 and 25 mg/l, preferably 5 - 15 mg/l, lie in the optimum range. Potential CO₂ damagings of fish and other water organisms do not occur here. Since CO₂ is continuously used up in the maintenance system and losses emerge into the atmosphere, CO₂ must be dosed in the correct amount to the maintenance water.

This can be achieved very easily by a daily or every two day dosing to be carried out of biologically decomposable organic compounds, e.g. of aliphatic organic carboxylic acids, alcohols and sugars. The following compounds have proved to be especially useful:

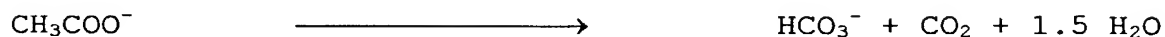
- a) carboxylic acids: formic acid, oxalic acid, acetic acid, lactic acid, citric acid, malic acid, tartaric acid,
- b) alcohols: ethanol, glycerol, sorbitol,
- c) sugars: pentoses, hexoses, saccharose.

If one doses the carboxylic acids alone, then, in a chemical reaction, from the hydrogen carbonate supply, the equivalent CO₂ amount is immediately liberated:



In the case of the subsequent biological breakdown of the carboxylic acid anion, the consumed hydrogen carbonate is

slowly again produced (within a few hours up to 24 hours) and further CO_2 formed:



Consequently, carboxylic acids produce CO_2 in a stepped process:

- a) in a secondary reaction by,protonisation of HCO_3^- ,
- b) in a reaction lasting a few hours up to 24 hours by oxidative biological breakdown.

Alcohols and sugars added to the maintenance system are subsequently broken down to H_2O and CO_2 in a relatively slow microbiological reaction.

By choice of combinations of different C-sources with different speeds of the CO_2 liberation, a very uniform CO_2 introduction can be achieved, e.g. by the combination of citric acid and saccharose or acetic acid and saccharose. The individual compounds or combinations are dosed as follows:

daily 1 - 20 mg/l, preferably 3 - 10 mg/l or also every 2 days 2 - 40 mg/l, preferably 6 - 20 mg/l.

The water improvement agent according to the invention can be used for the individually defined function purposes of use in all biological maintenance systems, such as e.g.

- The agent according to the invention is made available in the form of individual component products or a multiple component product, e.g. as packing for 100 to 1000 l of maintenance system, preferably as aqueous concentrate. The individual components 1.) to 4.) in the concentrate can hereby be combined in the amounts corresponding to the previously mentioned dosage recommendations. However, the individual components can also be packed individually or in compatible mixture in the single dose corresponding to the dosage amount or in larger amounts in solid form, e.g. as powder, granulates, extrudates, pearls, capsules or in tablet or liquid form. In this form, the individual partial problems can be solved individually or in any desired combination by addition of individual components or mixtures. Exact statements about the dosing of the concentrate individual components or mixtures are to be found in the packaging or on the leaflet in the packaging.

The dosing frequency is given from the functional use. It extends from daily over every two days and once or twice a week to once per two weeks or according to need.

Patent Claims

1. Process for the improvement of the water quality of biological maintenance systems, characterised in that one adds to the maintenance system individually or in any desired combination
 - a) for the lowering of the phosphate concentration, at least one easily or sparingly soluble Al^{3+} , Fe^{3+} , TiO^{2+} , ZrO^{2+} or Ca^{2+} salt of an organic carboxylic acid, possibly in admixture with an organic carboxylic acid;
 - b) for the lowering of the nitrate concentration or limitation of the nitrate increase, at least one water-soluble N-free, biologically decomposable organic compound;
 - c) for the increasing of the carbonate hardness or of the HCO_3^- concentration, at least one alkali metal or alkaline earth metal salt of a carboxylic acid;
 - d) for the increasing of the total hardness or of the concentration of Ca^{2+} and Mg^{2+} hydrogen carbonate, a mixture of at least one Ca^{2+} and Mg^{2+} salt of an organic carboxylic acid; and
 - e) for the increasing of the CO_2 concentration, at least one biologically decomposable compound.

2. Process according to claim 1, characterised in that, for the lowering of the phosphate concentration, one adds an Al^{3+} , Fe^{3+} , TiO^{2+} , ZrO^{2+} and/or Ca^{2+} acetate, formate, tartrate and/or especially citrate.
3. Process according to one of claims 1 and 2, characterised in that one adds weekly or two weekly 1 to 100, preferably 10 to 40 mg/l aluminium and/or iron (III) citrate.
4. Process according to claim 1, characterised in that, for the lowering of the nitrate concentration or limiting of the nitrate increase, one adds at least one aliphatic compound, .e.g. an alcohol, a sugar or a carboxylic acid.
5. Process according to claim 4, characterised in that one adds glycerol, sorbitol or ethanol, a pentose, a hexose or saccharose or acctic, citric, tartaric or lactic acid.
6. Process according to claim 4, characterised in that one adds a mixture of citric or acetic acid and saccharose or especially a mixture of citric acid, tartaric acid and saccharose.
7. Process according to one of claims 4 to 6, characterised in that every second day or three times weekly one adds 15 to 100, preferably 5 to 40 mg/l of the compound or the mixture.
8. Process according to claim 1, characterised in that, for the increasing of the carbonate hardness or of the HCO_3^-

concentration, one adds at least one alkali metal or alkaline earth metal salt of an aliphatic carboxylic acid.

9. Process according to claim 8, characterised in that one adds an alkali metal or alkaline earth metal salt of citric, acetic, lactic, tartaric, formic, propionic or malic acid.
10. Process according to claim 8, characterised in that one adds alkali metal and/or alkaline earth metal salt so much and so often that the desired carbonate hardness is achieved and remains maintained.
11. Process according to claim 1, characterised in that for the increasing of the total hardness or of the concentration of Ca^{2+} and Mg^{2+} hydrogen carbonates, one adds a mixture of Ca^{2+} and Mg^{2+} salts of organic carboxylic acids.
12. Process according to claim 11, characterised in that for the desired control of the composition of the total hardness, one adds further Ca^{2+} and Mg^{2+} chloride and/or sulphate.
13. Process according to claim 1, characterised in that for the increasing of the CO_2 concentration, one adds daily or every two days a carboxylic acid and/or an alcohol and/or a sugar.

14. Process according to claim 13, characterised in that one adds glycerol, sorbitol or ethanol, a pentose, a hexose or saccharose or acetic, citric or lactic acid.
15. Process according to one of claims 13 and 14, characterised in that one adds daily 1 to 20, preferably 3 to 10 mg/l or every two days 2 to 40, preferably 6 to 20 mg/l of the biologically decomposable compound or a mixture of such compounds.
16. Process according to claim 1, characterised in that one additionally introduces an amount of oxygen or hydrogen peroxide equivalent to the O_2 requirement of the maintenance system.
17. Single or multiple component product for the improvement of the water quality of biological maintenance systems for the functional, causal use according to need, characterised by a content (singly or in combination) of
 - 1) at least one easily or sparingly soluble Al^{3+} , Fe^{3+} , TiO^{2+} , ZrO^{2+} or Ca^{2+} salt of an organic carboxylic acid, possibly in admixture with an organic carboxylic acid;
 - 2) at least one water-soluble, N-free biologically decomposable organic compound;
 - 3) at least one alkali metal or alkaline earth metal salt of an organic carboxylic acid; and

- 4) a mixture of at least one Mg^{2+} and Ca^{2+} salt of an organic carboxylic acid.
18. Single or monocomponent product according to claim 17, containing singly or in combination
- 1) an Al^{3+} , Fe^{3+} , TiO^{2+} , ZrO^{2+} and/or Ca^{2+} acetate, formate, tartrate and/or especially citrate;
 - 2) glycerol, sorbitol or ethanol, a pentose, a hexose or saccharose or acetic, citric, tartaric or lactic acid;
 - 3) an alkali metal or alkaline earth metal salt of citric, acetic, lactic, tartaric, formic, propionic or malic acid; and
 - 4) a Ca^{2+} or Mg^{2+} salt or a mixture of Ca^{2+} and Mg^{2+} salts of organic carboxylic acids, possibly in admixture with Ca^{2+} and Mg^{2+} chlorides and/or sulphates.

Summary

A process is described for the improvement of the water quality or correction and adjustment of important chemical water parameters of biological maintenance systems, such as aquaria (warm water, cold water, fresh water, salt water), garden ponds, koi ponds, aquaterrains and large aquaria (zoos, public aquaria) in which one adds singly or in any desired combination

- a) for the lowering of the phosphate concentration, at least one easily or sparingly soluble Al^{3+} , Fe^{3+} , TiO^{2+} , ZrO^{2+} or Ca^{2+} salt of an organic carboxylic acid, possibly in admixture with an organic carboxylic acid;
- b) for the lowering of the nitrate concentration or limitation of the nitrate increase, at least one water-soluble, N-free, biologically decomposable organic compound;
- c) for the increasing of the carbonate hardness or of the HCO_3^- concentration, at least one alkali metal or alkaline earth metal salt of an organic carboxylic acid;
- d) for the increasing of the total hardness or of the concentration of Ca^{2+} and Mg^{2+} hydrogen carbonate, a mixture of at least one Ca^{2+} and Mg^{2+} salt of organic carboxylic acids; and
- e) for the increasing of the CO_2 concentration, at least one biologically decomposable compound and a single or multiple component product thereby usable.

Docket No. 6235-16-DCL



**COMBINED DECLARATION AND POWER
OF ATTORNEY IN ORIGINAL APPLICATION**

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are stated below next to my name; and that

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**TITLE: PROCESS FOR THE IMPROVEMENT OF THE WATER QUALITY OF
MAINTENANCE WATERS**

the specification of which

[] is attached hereto, or,
[X] was filed on March 11, 2002 as United States
(MM/DD/YY)

Application Number 10/088,049 or PCT International Application No. _____ and was amended on _____ (if applicable).
(MM/DD/YY)

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 C.F.R. § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119 (a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States listed below and have also identified below, by checking the box, any foreign application(s) for patent or inventor's certificate, or PCT International application having a filing date prior to that of the application on which priority is claimed.

Prior Foreign Application(s) (if any):

Number	Country	Filing Date	Priority Not Claimed
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19944799.3 Germany 09/18/1999 []
(MM/DD/YY)

Docket No. 6235-16-DCL

I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States provisional application(s) listed below:

Application No.

Filing Date

None

(MM/DD/YY)

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s) or § 365(c) of any PCT International application designating the United States listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application or the PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 C.F.R. § 1.56 which become available between the filing date of the prior application and the national or PCT international filing date of this application:

**Application
No.**

**Filing
Date**

**Status (Patented)
Pending, Abandoned)**

PCT/EP00/07980

August 16, 2000
(MM/DD/YY)

Pending

I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

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Docket No. 6235-16-DCL

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further, that these statements were made with knowledge that willful false statements and the like are punishable by fine or imprisonment, or both, pursuant to 18 U.S.C. § 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

1-00

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first inventor (given name,
family name)

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First Inventor's signature

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